991320

# PATENT SPECIFICATION

NO DRAWINGS

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**Int. Cl.:**—C 07 c, d // B 29 d, C 07 g, C 08 f, g, C 09 b, d, C 11 b, G 02 d

COMPLETE SPECIFICATION

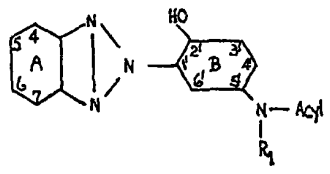
## Improvements relating to the Stabilisation of Light and Oxidation Sensitive Organic Materials

We, J. R. GEIGY A.—G., a body corporate organised according to the laws of Switzerland, of 215, Schwarzwaldallee, Basle, Switzerland, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention concerns the use of 2 - ($2^1$ - hydroxy - $5^1$ - acylaminophenyl)-benztriazole compounds for the stabilisation of light and oxidation sensitive organic materials to the injurious effect of light and oxidising agents as well as, as industrial product, the organic materials protected against the influence of light and oxidising agents.

It has been found that organic material which is sensitive to light and oxidation can be protected from the effect of light and oxidising agents by incorporating into the organic materials at least one 2-($2^1$-hydroxy-$5^1$-acylaminophenyl)-benztriazole compound.

The active ingredients correspond to the general formula I.




(I)

In this formula:

"Acyl" represents an organic acyl radical and

$R_1$ represents hydrogen or an alkyl, alkenyl, cycloalkyl or aralkyl radical which can be substituted by a carboxy or a carbalkoxy group; $R_1$ and "Acyl" together with the nitrogen atom can also form a ring and, in this case,

$R_1$ is a carbonyl group or a methylene group possibly substituted by alkyl groups, and wherein

the nucleus A can be substituted in the 4-, 5- and 6-positions by alkyl, alkoxy, carboxyl, carboxylic acid ester, carboxylic acid amide, sulphonic acid amide, alkyl sulphonyl groups or halogens, and

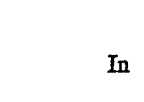
the nucleus B can be substituted in the $3^1$- and $4^1$-positions by alkyl, cycloalkyl, aralkyl and aryl groups, or halogens.

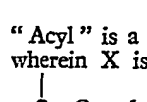
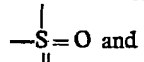
Thus, the benzene ring A can contain in the 4-, 5- or 6-position alkyl groups having 1 to 6 carbon atoms, e.g., methyl, ethyl, isobutyl groups, alkoxy groups, e.g., methoxy or butoxy groups, halogens, e.g., chlorine or bromine, carboxyl groups, carboxylic acid ester groups preferably carboxylic acid alkyl ester groups, e.g., carbomethoxy, carboethoxy, carbopropoxy or carbobutoxy groups, carboxylic acid or sulphonic acid amide groups possibly aliphatically, cycloaliphati-

[*Price 4s. 6d.*]

PRICE 75p

cally, araliphatically or aromatically substituted at the nitrogen atom and wherein two aliphatic substituents together with the amino nitrogen atom and possibly with the inclusion of a further hetero atom can form a heterocyclic ring, e.g., carboxylic acid or sulphonic acid amide, methylamide, ethylamide, butylamide, cyclohexylamide, benzylamide, dimethylamide, diethylamide, N-methyl-N-cyclohexylamide, γ-methoxypropylamide, piperidide or morpholide groups as as well as alkylsulphonyl groups, e.g., methylsulphonyl or ethylsulphonyl groups. The benzene ring B can be substituted in the 3¹- and 4¹-positions by alkyl groups, e.g., methyl, ethyl, tert. butyl groups; aralkyl groups, e.g., benzyl groups, cycloalkyl groups, e.g., cyclohexyl groups or aryl groups, e.g., phenyl groups, or halogens, e.g., chlorine or bromine.

In the group  ,

"Acyl" is a radical of the formula  wherein X is a carbon atom or the radical  and

Y is an oxygen atom or, if X is a carbon atom, a sulphur atom, or Y can be an imino group which with X and $R_2$ forms an s-triazine or pyrimidine ring.

$R_2$ represents an alkyl, alkenyl, cycloalkyl, aralkyl or an aryl group wherein the aryl group can be substituted, e.g., by halogen atoms, alkoxy, alkyl, free or modified carboxyl groups and, particularly if X is a carbon atom, $R_2$ is an alkyl group which can be further substituted by halogen atoms, etherified mercapto groups, free or etherified hydroxy groups, primary, secondary or tertiary amino groups and free or modified carboxyl groups,

or, if X is a carbon atom, $R_2$ also represents hydrogen,

or an alkoxy, alkenyloxy, cycloalkyloxy, aralkyloxy, or an aryloxy group wherein the aryl radical of the aralkoxy or aryloxy group can be substituted, e.g., by alkyl, alkoxy groups or halogen atoms and the alkyloxy group can be substituted by alkoxy or alkylmercapto groups,

or an amino group which can be substituted at the nitrogen atom by one or two identical or different alkyl, alkenyl, cycloalkyl, aralkyl or aryl groups,

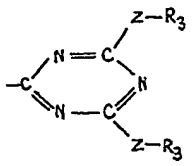
or an imino group of a saturated monocyclic heterocycle,

or, if $R_1$ and $R_2$ are linked together, together with X and $R_1$, it represents the remainder of a lactam or dioxopyrrolidine ring.

In every case, the olefinic double bond of the alkenyl group which may be present is separated from the next hetero atom by at least one carbon atom and the hetero atoms bound to saturated carbon atoms are separated from the next hetero atom by at least one further carbon atom.

Preferably "acyl" represents the following groups; the preferred number of carbon atoms of this group is given in brackets.

a) An s-triazinyl radical of the formula

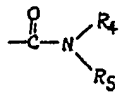


wherein Z represents an imino or an alkylimino group ($C_{1-8}$), an oxygen or sulphur atom, and

$R_3$ represents an alkyl group ($C_{1-12}$), cycloalkyl group ($C_{5-8}$), or an aralkyl group ($C_{7-12}$), whilst $R_3$ together with the alkylimino group can form a 5 to 7 membered, saturated heterocyclic ring (and the whole group contains at most 25 carbon atoms),

b) a pyrimidyl radical which contains in the ring at most one CH— group and which is substituted at the other carbon atoms by chlorine and at most one $ZR_3$— group (and the whole group contains at most 17 carbon atoms),

c) a carbamoyl radical of the formula

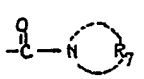


wherein

$R_4$ and $R_5$ independently of each other represent hydrogen or an $R_6$-group ($R_4$ and $R_5$ together contain at most 19 carbon atoms), and

$R_6$ represents an alkyl group ($C_{1-18}$), an alkenyl group ($C_{2-7}$), a cycloalkyl group ($C_{5-8}$), an aralkyl group ($C_{7-12}$), an aryl group ($C_{6-10}$), which can be substituted in particular by halogen atoms, alkoxy, alkyl, free or modified carboxyl groups,

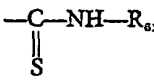
d) a carbamoyl radical of the formula



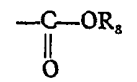
wherein

$R_7$ represents an alkylene radical ($C_{4-8}$) or an oxalkylene radical ($C_{4-6}$) which together with the nitrogen atom forms a 5 to 7 membered saturated heterocyclic ring,

e) a thiocarbamoyl radical of the formula



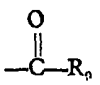
f) a carbonic acid monoester radical of the formula



wherein

$R_8$ has the same meaning as $R_6$ and in addition, it represents an alkoxyalkyl radical ($C_{2-10}$), a halogenalkyl radical ($C_{1-5}$), or an alkylmercaptoalkyl radical ($C_{3-10}$),

g) a carboxylic acid radical of the formula



wherein

$R_9$ has the same meaning as $R_8$ and in addition it represents hydrogen or an alkenyl radical ($C_{6-18}$), a carboxyalkyl radical ($C_{2-10}$), a carboxyaryl radical ($C_7$), carboxyalkenyl radical ($C_{4-6}$), a carbalkoxyalkyl radical ($C_{7-11}$), a carboxyalkoxy alkyl radical ($C_{6-9}$), a carboaralkyloxyalkyl radical ($C_{8-14}$), a carboaryloxyalkyl radical ($C_{8-14}$), an $R_6$-O-alkyl radical ($C_{2-22}$), an $R_6$-S-alkyl radical ($C_{2-22}$), an $R_1$>N-alkyl radical ($C_{2-22}$), an alkylene $R_5$ radical ($C_{4-8}$), or an oxalkylene radical ($C_{4-8}$), or

h) a sulphonic acid radical of the formula $-SO_2R^1$ wherein $R^1$ has the meaning given for $R_6$.

If $R_3$ to $R_9$ are aryl radicals then they are preferably monocyclic.

$R_1$ is preferably hydrogen, an unsubstituted alkyl group ($C_{1-18}$), a carboxyalkyl group ($C_{2-5}$), a carbalkoxyalkyl group ($C_{3-14}$), a cycloalkyl group ($C_{5-8}$) or an aralkyl group ($C_{7-12}$).

If $R_1$ and $R_2$ are bound together, $R_1$ is preferably a carbonyl or a methylene group and $R_2$ is a 1,2-ethylene group. Preferably $R_1$ and the "acyl" radical together contain at most 26 carbon atoms, at most 5 nitrogen atoms, at most 4 oxygen atoms and at most 2 sulphur atoms.

Benztriazole compounds which absorb at particularly long wave lengths are obtained if there are acidifying substituents in the ring A. Benztriazole compounds having particularly high molar extinction in the range of 330—350 mμ are obtained if there are basifying substituents in the 5- and/or $4^1$-position. Sometimes the molar absorption in the range of 300 mμ is promoted by further substituted alkyl substituents in the $3^1$-position. Examples of basifying substituents are alkoxy groups, e.g., the methoxy, isopropoxy, cyclohexyloxy and benzyloxy group; examples of acidifying substituents are the alkylsulphonyl groups, e.g., the methyl and ethyl sulphonyl group, sulphonic acid amide groups, e.g., the sulphonic acid methylamide, butylamide and cyclohexylamide group, as well as the carboxyl group and its esters or amides.

Naturally, typical dyestuff groups, e.g., aromatic azo groups, anthraquinone groups containing auxochromes or phthalocyanine groups, are to be excluded as substituents from the benztriazole compounds according to the invention.

The 2 - ($2^1$ - hydroxy - $5^1$ - acylaminophenyl)-benztriazole compounds which can be further substituted as defined for A and B in formula I can be produced, for example, by one of three different methods: by oxidative ring closure of 2 - amino - $2^1$ - hydroxy-$5^1$-acylamino-$1,1^1$-azobenzene compounds with salts of divalent copper in a neutral to alkaline medium; by reductive ring closure of 2 - nitro - $2^1$ - hydroxy - $5^1$ - acylamino-$1,1^1$-azobenzenes, e.g., with zinc dust in an alkaline medium; by modification of functional groups in the completely formed 2-phenylbenztriazole compound, either by acylation of the amino group in 2-($2^1$-hydroxy - $5^1$ - aminophenyl) - benztriazole compounds, or by liberation of the hydroxyl group in the $2^1$-position of a 2-($2^1$-alkoxy-$5^1$-acylaminophenyl)-benztriazole compound by dealkylation or liberation of such a group in a 2 - ($2^1$ - acyloxy - $5^1$ - acylaminophenyl)-benztriazole compound by saponification. The dealkylation can be performed, for example, in boiling benzene with aluminium chloride, the saponification by heating with a solution of alkali hydroxides in a mixture of water and an alcohol, e.g. with a mixture of concentrated aqueous caustic soda lye and ethylene glycol monomethyl ether.

To introduce the "acyl" radical, e.g. the carboxylic acid radical of the formula $R_2$—CO— into the starting materials usable according to the invention, acylating agents are used, e.g. anhydrides esters, e.g. esters of alkanols having 1 to 6 carbon atoms and preferably, halides, in particular chlorides, or also ketenes of carboxylic acids corresponding to $R_2$—CO—; to introduce a carbonic acid monoester radical of the formula $R_8$—OCO—, a sulphonic acid radical of the formula $R_6$—$SO_2$— or a cyclic carbonic acid imide radical, in particular a 1,3,5-triazinyl-(2) radical, the halides, chiefly the chlorides, of the corresponding acids are used.

To introduce a carbamoyl or thiocarbamoyl radical either the halides of the corresponding acids are used or, advantageously, iso-

cyanates or mustard oils, for example, phenyl isocyanate or phenyl mustard oil.

The 2 - ($2^1$ - hydroxyphenyl) - benztriazole compound containing an acylatable amino group in the $5^1$-position is reacted with the acylating agent by heating, possibly in inert organic solvents, e.g. in halogenated or nitrated aromatic hydrocarbons, for example in benzene, toluene, chlorobenzene or nitrobenzene, or also in a tertiary amine, e.g. in pyridine or diethyl aniline. In every case, care should be taken that the hydroxyl group in the $2^1$-position is not acylated. This is done by performing the reaction in a weakly acid to weakly alkaline medium.

If the compounds of formula I contain reactive groups, these can subsequently be converted by further reactions into other groups. Thus, for example, mobile halogen in halogen fatty acid amide groups can be exchanged for the corresponding alkoxy, mercaptide, amino or cyano group by reaction with alcohols, mercaptans, primary or secondary amines or alkali cyanides; or carboxyl or sulphonic acid groups can be converted by way of the acid chloride into corresponding acid ester or amide groups; or alcohols, mercaptans, amines or hydrocyanic acid can be added at suitable double bonds.

Examples of such subsequent modifications are the replacement of the chloride atom in 2 - ($2^1$ - hydroxy - $5^1$ - $\beta$ - chloropropionylamino - $3^1$ - methylphenyl) - benztriazole by diethylamine, cyclohexylamine, benzylamine and N-methylcyclohexylamine, to form 2-($2^1$-hydroxy - $5^1$ - $\beta$ - diethylaminopropionylamino - $3^1$ - methylphenyl) - benztriazole, 2 - ($2^1$ - hydroxy - $5^1$ - $\beta$ - cyclohexylaminopropionylamino - $3^1$ - methylphenyl) - benztriazole, 2 - ($2^1$ - hydroxy - $5^1$ - $\beta$ - benzylaminopropionylamino - $3^1$ - methylphenyl)-benztriazole and 2 - ($2^1$ - hydroxy - $5^1$-$\beta$ - methylcyclohexylaminopropionylamino-$3^1$ - methylphenyl)-benztriazole, or the addition of octylmercaptan to 2-($2^1$-hydroxy-$5^1$ - acryloylmethylamino - $3^1$ - chlorophenyl) - 5 - ethylbenztriazole to form 2-($2^1$ - hydroxy - $5^1$ - $\beta$ - octylmercaptopropionylmethylamino - $3^1$ - chlorophenyl)-5-ethylbenztriazole.

Depending on the way in which they are substituted, the substituted 2-($2^1$-hydroxy-$5^1$-acylaminophenyl)-benztriazole compounds are colourless to pale yellowish coloured. They absorb UV light and, at the same time, have an antioxidant effect which differentiates them from the related 2-($2^1$-hydroxyphenyl)-benztriazole compounds having acylamino groups in the $4^1$- or -5- position. They also have good fastness to sublimation and are suitable as stabilisers which absorb at long wave lengths.

As regards solubility and facility in working up, those acylamino-2-($2^1$-hydroxyphenyl)-benztriazole compounds usable according to the invention are preferred the acylamino groups of which are derived from a secondary amine. The fastness to light generally increases in the following order: triazinylamino→carboxylic acid amido→sulphonic acid amido compounds; i.e. the more acid the free acid corresponding to the acyl radical is, the better is the fastness to light.

The stabilisers according to the invention are incorporated into the materials to be protected in amounts of 0.001—5% by weight, in particular in amounts of 0.01—1% by weight calculated on the carrier.

The main carriers for the 2-($2^1$-hydroxy-$5^1$ - acylaminophenyl) - benztriazole compounds are polymers e.g. completely synthetic polymers, e.g. addition polymers, in particular polymers of compounds having vinylene double bonds, e.g. those of vinyl chloride, vinylidene chloride, styrene, dienes e.g. butadiene, isoprene, ethylene, propylene, acrylic compounds e.g. acrylonitrile or methyl methacrylate as well as copolymers thereof; condensation polymers e.g. polyesters, e.g. polyethylene glycol terephthalate, or polyamides, e.g. polycaprolactam, or mixed polymers i.e. polycondensates and polyaddition compounds e.g. polyester resins; in addition, natural polymers or synthetic modifications thereof, e.g. cellulose, cellulose esters and ethers and proteins. Non-polymeric carriers can also be employed, e.g. fats, oils or waxes. The molecular weight of the polymers mentioned above plays a subsidiary role as long as it lies within the margins necessary for the characteristic properties of the polymers concerned. Depending on the polymers, it can be between 1000 and several millions.

In non-polar polymers, those benztriazole compounds are particularly suitable which, in addition to the hydroxyl group present as defined, have as few as possible polar groups e.g. carboxylic acid and sulphonic acid amide groups, in particular those of primary amines. In this case, generally products having a low melting point are preferred because of their solubility.

In general, it is recommended that the possible use of a specific product be estimated by solubility trials. For example, if the product is difficultly soluble, even hot, in the solvents known for the polymers to be protected, then unfavourable results in this polymer are to be expected.

The new substituted 2-($2^1$-hydroxyphenyl)-benztriazole compounds are incorporated into these polymers—depending on the type of polymer—, e.g. by working in at least one of these compounds and, possibly, other additives e.g. plasticisers, antioxidants, heat stabilisers and pigments, into the melts before or during moulding by the methods usual in the industry, or by dissolving them in the corresponding monomers before polymerisa-

tion provided they do not interact with the monomers, or by dissolving the polymers and the additives in solvents and subsequently evaporating off the latter. The new substituted 2 - ($2^1$ - hydroxyphenyl) - benztriazole compounds can also be drawn onto films or threads from baths, e.g. from aqueous dispersions.

The light sensitive materials can also be protected from the injurious effect of light by painting them with a protective coating—e.g. a lacquer—containing at least one compound as defined of the formula I, or by covering them—advantageously with film-like covers—which contain such stabilisers. In both these cases, the amount of stabiliser to be added is advantageously 10—30% by weight (calculated on the protective coating material) for protective coatings of less than 0.01 mm thickness and 1—10% by weight for coatings of 0.01—0.1 mm thickness. The benztriazole derivatives according to the invention are all the more valuable the more colourless they are as otherwise they lend a yellow shading to the finished product.

For certain types of use, particularly if warm chips have to be powdered, products which melt above the softening temperature of the polymer concerned and, in spite of this are sufficiently soluble in the melted polymers, are particularly valuable.

In general, the more colourless and the less they change colour on exposure to oxygen, the more valuable are the benztriazole derivatives.

The following Examples illustrate the invention. Where not otherwise stated, parts are given as parts by weight. The temperatures are given in degrees Centigrade. The relationship of parts by weight to parts by volume is as that of kilogrammes to litres.

EXAMPLE 1.

100 Parts of a usual marketed liquid polyester resin consisting of 70% polycondensate of maleic acid, phthalic acid and ethylene glycol, and 30% by weight of styrene are mixed with 0.3 parts of 2-($2^1$-hydroxy-$5^1$-N-$\beta$ - carbobutoxyethylbenzoylaminophenyl)-benztriazole and 1 part of benzoyl peroxide. The mixture is poured into a mould and cured by heating for 3 hours at 80°. The 2 mm thick, colourless, transparent polyester resin plate formed absorbs all UV light of wave lengths less than 380 m$\mu$ and can be used as UV filter.

Polyester resin plates stabilised to discolouration due to the effect of light are produced in an analogous manner if, instead of the styrene, an equivalent amount of methyl methacrylate is used.

If instead of maleic acid, 1,4,5,6,7,7-hexachlorobicyclo - 5 - heptene - 2,3 - dicarboxylic acid (Het acid) is used, then flame resistant polyester resins are obtained which absorb UV light well are obtained.

Such polyester plates are suitable as roofing material. In addition, other compounds mentioned in the production Examples I to XVI can also be used, according to their solubility, as stabilisers.

EXAMPLE 2.

The autoxidation of the petroleum distillate used as standard test oil and termed "Regal Oil B" (produced by Texas Oil Co. USA) was determined in the so-called "Continental Oil Oxidation Test," with and without the addition of stabilisers, as described in Ind. & Eng. Chemistry, *33*, 339 (1941). The time is given below after which the oxygen pressure has been reduced by 60 mm Hg due to oxygen take-up caused by autoxidation.

| Additive | Duration of test until 60 mm reduction in pressure |
|---|---|
| none | 50 hours |
| 2 - ($2^1$ - hydroxy - $5^1$ - acetylaminophenyl)-benztriazole (0.025% by weight) | 182 hours |
| 2 - ($2^1$ - hydroxy - $5^1$ - butyrylaminophenyl)-benztriazole (0.025% by weight) | 150 hours. |

Similar results are obtained if, instead of the compounds mentioned, 0.075% by weight of 2 - ($2^1$ - hydroxy - $5^1$ - ($4^{11}$,$6^{11}$ - bis - dibutylamino - $1^{11}$,$3^{11}$,$5^{11}$ - triazinyl - ($2^{11}$)-aminophenyl) - benztriazole or 2 - ($2^1$-hydroxy - $5^1$ - caproylaminophenyl) - 5-chlorobenztriazole are used to inhibit autoxidation.

In addition the other compounds mentioned herein in the production Examples I to XVI can also be used, according to their solubility, as stabilisers.

EXAMPLE 3.

A mixture consisting of
65 parts of polyvinyl chloride (Lonza A.G. Basle),
32 parts of dioctyl phthalate,
2 parts of barium/cadmium laurate, and
0.5 parts of 2-($2^1$-hydroxy-$5^1$-caproyl-aminophenyl)-5-chlorobenztriazole

is calendered on a set of mixing rollers at 150° to form a film of 0.1 mm thickness. It absorbs UV light and can be used as packing material for materials which are sensitive to UV light. The transmission of UV light at 360 mμ is less than 6%.

Similar results are obtained if, instead of the compound mentioned, 0.5 parts of
2 - ($2^1$ - hydroxy - $5^1$ - N - benzylacetamino-phenyl)-benztriazole,
2 - ($2^1$ - hydroxy - $5^1$ - carbocyclohexyloxy-benzylaminophenyl) - 5 - ethylsulphonyl-benztriazole, or
2 - ($2^1$ - hydroxy - $5^1$ - β - carbobutoxy-propionylaminophenyl) - 5 - carbo-butoxy-benztriazole

are used.

Copolymers from polyvinyl chloride and polyvinyl acetate can be worked up in the same way into UV dense films.

In addition other compounds mentioned in the production Examples I to XVI can be used, according to their solubility, as stabilisers.

EXAMPLE 4.

Cellulose-acetobutyrate films which do not transmit UV light are prepared by drawing onto glass a solution of 150 parts of Cellit BF—900 (Cellulose-acetobutyrate of Farben-fabriken Bayer AG., Leverkusen, Germany), 20 parts of dibutyl phthalate, 800 parts of acetone and 0.35 parts of 2-($2^1$-hydroxy-$5^1$-butyrylaminophenyl)-benztriazole. "Cellit" is a Registered Trade Mark.

After evaporating off the solvent, a colourless film of 0.4 mm thickness is obtained which substantially absorbs all UV light in the wave lengths below 380 mμ. It is excellently suitable as protective film, for example, for use in shop windows.

Instead of the acetobutyrate, cellulose acetate or propionate can be used with similar results.

Similar results are obtained if instead of the compound mentioned, 0.4 parts of 2-($2^1$-hydroxy - $5^1$ - carbobenzyloxyaminophenyl)-benztriazole are used.

In addition, other compounds mentioned in the production Examples I to XVI can also be used, according to their solubility as stabilisers.

EXAMPLE 5.

100 Parts of polyethylene powder (DFD 4400 of Union Carbide International Chemical Co. 30 East 42nd St. New York, NY, USA) are mixed with 0.25 parts of the compound 2 - ($2^1$ - hydroxy - $5^1$ - benzoyl - $\beta^1$ - carbo-decyloxyethylaminophenyl)-benztriazole and the mixture is blown from an extruder into a foil of about 0.06 mm thickness.

The film absorbs UV light and can be used as a protection, e.g. for covering greenhouses.

If instead of polyethylene, polypropylene (Profax 6512 of Hercules Powder Co., Wilmington, Delaware USA) is used then, on using an extruder fitted with a slit die at 250—270°, a UV absorbent polypropylene film of high transparency in the visible range can be obtained. "Profax" is a Registered Trade Mark.

Similar results are obtained, if instead of the substance mentioned, 0.3 parts of:
2 - ($2^1$ - hydroxy - $5^1$ - N - cyclohexyl-benzoylaminophenyl - benztriazole or
2 - ($2^1$ - hydroxy - $5^1$ - N - butyl-benzoylaminophenyl) - benztriazole are used.

In addition, other compounds mentioned in the production Examples I to XVI can also be used, depending on their solubility, as stabilisers.

EXAMPLE 6.

100 Parts of granulated Nylon 66 (produced by condensation of hexamethylenediamine and adipic acid in molecular ratio 1:1 at about 265° while excluding oxygen) and 0.5 parts of 2 - ($2^1$ - hydroxy - $5^1$ - acetylamino-phenyl)-benztriazole are mixed in a dry state and extruded into a continuous film. The film absorbs UV light and is suitable as UV-absorbant packing material. If, instead of Nylon 66, Nylon 6 or 11 or the mixed condensate 6/10 is used, then films having very similar optical properties are obtained.

Similar results are obtained if instead of the substance mentioned, 0.7 parts of:
2 - ($2^1$ - hydroxy - $5^1$ - caproylaminophenyl)-5 - methyl - benztriazole, or 2 - ($2^1$-hydroxy - $5^1$ - caproylaminophenyl) - 5-methoxy - 6 - methyl - benztriazole are used.

In addition, other compounds mentioned in the production Examples I to XVI can also be used, depending on their solubility, as stabilisers.

EXAMPLE 7.

100 Parts of methyl methacrylate, 0.2 parts of 2 - ($2^1$ - hydroxy - 5 - p - methyl-benzoylbenzylaminophenyl) - benztriazole and 0.2 parts of lauroyl peroxide are mixed and polymerised at 70° between glass plates into a plate of 2 mm thickness. The plate obtained absorbs substantially all UV light between 270 and 380 mμ. The transmission of the UV light only changes very slightly when the plate is exposed for 1000 hours in the fadeometer.

In addition, other compounds mentioned in the production Examples I to XVI can also be used, depending on their solubility, as stabilisers.

EXAMPLE 8.

100 Parts of polyacrylonitrile (produced by polymerisation of acrylonitrile according to W. R. Sorenson and T. W. Campbell, "Preparative Methods of Polymer Chemistry, Interscience Publishers Inc., New York 1961) and 0.5 parts of 2-(2¹-hydroxy-5¹-methane sulphonic acid heptylamidophenyl)-5-chlorobenztriazole are mixed and the mixture is suspended in 1000 parts of greatly cooled dimethyl formamide while stirring well. The dispersion obtained is rolled, first for 2 hours in a wide-necked screw cap bottle at room temperature and then at 50° until a homogeneous dope is obtained. A film is cast therefrom on a glass plate. The solvent is slowly evaporated at 80° in a forced draught oven thus yielding a transparent film. This film substantially absorbs all UV light from 270 to 370 mμ.

Similar UV dense films are obtained in the same way from a copolymer consisting of 90% by weight acrylonitrile and 10% by weight vinyl acetate.

Further compounds named in Examples I to XVI can be used, according to their solubility, for the stabilisation of the above polymers.

EXAMPLE 9.

100 Parts of polystyrene (Shell Petrochemicals Ltd., England) and 0.3 parts of 2-(2¹ - hydroxy - 5¹ - carbocyclohexyloxymethylaminophenyl)-benztriazole are well mixed and extruded at 240° to form 2 mm thick plates. These plates absorb more than 99% of the UV light from 270—370 mμ and are less prone to yellowing on exposure to light than plates prepared similarly but without addition of the light protecting agent.

Further compounds named in Examples I to XVI can be used, according to their solubility, for the stabilisation of the polystyrene.

EXAMPLE 10.

100 Parts of commercially available polyethylene glycol terephthalate (Terlenka, Allgemeene Kunstzijde Unie, Arnhem, Holland) and 1 part of 2-(2¹-hydroxy-3¹-propyl-5¹-pentane carboxylic acid amidophenyl)-benztriazole are mixed as dry powders and, after thorough drying, extruded at 285° into a continuous film of approximately 0.2 mm thickness. The transparent, almost colourless film absorbs more than 90% of the UV light between 270 and 380 mμ. It is useful as a UV dense wrapping material. "Terlenka" is a Registered Trade Mark.

Further compounds named in Examples I to XVI can be used, according to their solubility, for the stabilisation of polyethylene glycol terephthalate.

EXAMPLE 11.

A polyvinyl butyral sheet (produced by acetalisation of polyvinyl alcohol with butyraldehyde) is immersed for 3 minutes in a solution of 8 parts of 2-[2¹-hydroxy-5¹-(4¹¹,6¹¹ - bis - dibutylamino - s - triazinyl-(2¹¹)) - aminophenyl] - benztriazole in 100 parts by volume of benzene. After drying, the sheet is used to bond two glass plates at 140° under pressure. The safety glass plates so obtained can be used as UV dense glass windows in automobile construction. In addition, the organic binder has less tendency to yellowing than that of a safety glass plate prepared with a polyvinyl buyral sheet containing no light stabilising agent.

Further compounds named in Examples I to XVI can be used, according to their solubility, for the stabilisation of polyvinyl butyral.

The benztriazole compounds mentioned in this and the above Examples 1 to 10 as well as 5¹ - acylamino - benztriazole derivatives which can be used in a similar manner, are prepared in the following way:

*I.*

279 Parts of *o*-nitroaniline are stirred overnight in 1000 parts by volume of water. The next morning, 600 parts by volume of concentrated hydrochloric acid are added and the mixture is diazotised at 0—5° by the dropwise addition of 140 parts of sodium nitrite dissolved in 300 parts by volume of water in such a way that there is always a slightly positive reaction to nitrite paper. The clear diazo solution obtained is added dropwise at 0—5° to a solution prepared by suspending 302 parts of N-acetyl-*p*-aminophenol in 2000 parts by volume of water and adding concentrated sodium hydroxide solution until the pH is 11, the pH of the reaction solution being simultaneously always kept at 11 by the addition of concentrated sodium hydroxide solution. The 2-nitro-2¹-hydroxy-5¹-acetylaminoazobenzene formed separates immediately in the form of a dark rust brown powder and, when the addition of the diazo solution has been completed, it is filtered off under suction and washed with cold water. The moist filter residue is stirred with 3000 parts by volume of 3 N sodium hydroxide solution and, at 0—10°, 600 parts of zinc dust are added in portions. The azo compound gradually becomes decoloured and the colour of the suspension formed changes to yellow-red. The temperature of the mixture is then raised to room temperature and it is stirred for 3 hours at this temperature. The zinc sludge is then filtered off in an atmosphere of nitrogen and the filtrate is stirred into 6000 parts of 3 N hydrochloric acid. The

reaction product which precipitates is filtered off under suction and after washing well with water is dried and then recrystallised from dimethyl formamide. The 2-(2¹-hydroxy-5¹-acetylaminophenyl)-benztriazole so obtained is in the form of yellowish needles and melts at over 260°. Because of its difficult solubility in lipophilic solvents, this product is suitable as stabiliser only for strongly polar substrata such as, e.g. Nylon.

595 Parts of the above acetylaminobenztriazole, 6000 parts by volume of methyl cellosolve ("Cellosolve" is a Registered Trade Mark) and 3000 parts by volume of concentrated hydrochloric acid are refluxed for 3 hours. After one hour, a clear solution is formed in which, after 75 minutes, a solid precipitate forms. Vigorous stirring is thus indicated. The suspension obtained is stirred overnight at room temperature and then filtered. The filter residue is dissolved hot with 3500 parts by volume of a 2:1 mixture of methyl cellosolve and water and clarified with animal charcoal whereupon 1000 parts of sodium acetate are added to the filtrate when it is still hot. Yellow crystals quickly form which, after cooling, are filtered off under suction and washed with water. Yield: 405 parts. Recrystallisation from ethyl alcohol/water produces 2-(2¹-hydroxy-5¹-aminophenyl)-benztriazole in the form of deep yellow crystals which melt at 178°.

The following products are produced in an analogous manner:

2 - (2¹ - hydroxy - 5¹ - acetylaminophenyl)-5-chlorobenztriazole,

2 - (2¹ - hydroxy - 5¹ - acetylaminophenyl)-5-methylbenztriazole,

2 - (2¹ - hydroxy - 5¹ - acetylaminophenyl)-5-methoxybenztriazole,

2 - (2¹ - hydroxy - 3¹ - methyl - 5¹ - acetylaminophenyl) - benztriazole - 5-carboxylic acid,

2 - (2¹ - hydroxy - 4¹ - methyl - 5¹ - acetylaminophenyl) - 5 - ethylsulphonyl-benztriazole.

2 - (2¹ - hydroxy - 5¹ - acetylaminophenyl)-benztriazole - 5 - sulphonic acid - N-methylcyclohexylamide.

In the production of azo compounds derived from very weakly basic amines which compounds are preferably diazotised with nitrosyl sulphuric acid, the coupling is advantageously performed in glacial acetic acid, sodium acetate being used as acid binding agent.

The free amines forming the basis of the compounds mentioned are obtained by saponification according to the method described, with the exception of 2-(2¹-hydroxy-5¹ - aminophenyl) - 5 - methoxybenztriazole as, under the conditions described, the methoxyl group is split off.

*II.*

13 Parts of 2-(2¹-hydroxy-5¹-aminophenyl)-5-chloro-benztriazole (M.P. 169°, produced according to Example I) are suspended in 100 parts of dimethyl aniline and 50 parts of chlorobenzene and 7.4 parts of caproic acid chloride are added dropwise at about 30°. The thick paste obtained is slowly heated and at about 150° a clear solution is obtained. The reaction mixture is allowed to cool while stirring. The product which crystallises out is filtered off under suction and well washed with methanol to remove a few greenish blue impurities. It is further purified by recrystallising from dimethyl formamide-methyl cellosolve. 14.7 Parts of 2-(2¹-hydroxy-5¹-pentane carboxylic acid amidophenyl)-5-chlorobenztriazole are obtained, M.P. 237°.

The following products are obtained in an analogous manner:

2 - (2¹ - hydroxy - 3¹ - methyl - 5¹ - pentane carboxylic acid amidophenyl) - benztriazole,

2 - (2¹ - hydroxy - 3¹ - propyl - 5¹ - pentane carboxylic acid amidophenyl) - benztriazole,

2 - (2¹ - hydroxy - 3¹ - chloro - 5¹ - pentane carboxylic acid amidophenyl) - 5-ethylsulphonyl-benztriazole,

2 - (2¹ - hydroxy - 3¹ - cyclohexyl - 5¹-pentane carboxylic acid amidophenyl)-benztriazole-5-carboxylic acid,

2 - (2¹ - hydroxy - 5¹ - pentane carboxylic acid amidophenyl)-5-methoxy-6-methyl-benztriazole, (the starting material is obtained by coupling 2-hydroxy-5-nitrophenyl diazonium chloride with 3-methoxy-4-methyl aniline, then closing the ring with copper sulphate in basic ammonia solution and catalytically reducing the nitro group with Raney nickel), and

2 - (2¹ - hydroxy - 3¹ - cyclohexyl - 5¹-pentane carboxylic acid amidophenyl)-benztriazole-5-sulphonic acid diethylamide,

2 - (2¹ - hydroxy - 5¹ - pentane carboxylic acid amidophenyl) - benztriazole - 5-carboxylic acid dibutylamide.

*III.*

79.6 Parts of *p*-*β*-carboxypropionylbutylaminophenol (obtained by reacting succinic acid anhydride with N-butyl-*p*-aminophenol) are pasted in 300 parts of water. On adding concentrated sodium hydroxide solution, until the pH is 11, a solution is obtained. A diazo solution, produced from 41.4 parts of *o*-nitraniline according to Example 1, is added dropwise to this solution at 0—5° in such a way that excess diazonium salt can never be traced. The pH of the reaction solution is kept at 11—11.5 by simultaneous addition of concentrated sodium hydroxide solution. On completion of the addition of the diazo solution the reaction mixture is stirred for half an hour. 100 parts of solid sodium hydroxide are then added followed by 100 parts of zinc dust which are sprinkled in portions in the

solution. After the addition of the zinc, another 100 parts of solid sodium hydroxide are added the temperature being kept at 27°. The reaction mixture becomes decoloured and is stirred for half an hour whereupon it is stirred into a mixture of 1000 parts of water and 500 parts by volume of concentrated hydrochloric acid. The dark coloured precipitate, after stirring for one hour at room temperature, is filtered off under suction, washed with water and dried. The product is recrystallised from a mixture of ligroin and chlorobenzene with the addition of animal charcoal. To purify further it is recrystallised from toluene. The 2 - ($2^1$ - hydroxy-$5^1$ - $\beta$ - carboxypropionylbutylaminophenyl)-benztriazole so obtained melts at 154°. It can be used direct as a light stabiliser or, after conversion into the acid chloride with thionyl chloride, it can be converted into the following esters by boiling with the corresponding alcohol:

2 - ($2^1$ - hydroxy - $5^1$ - $\beta$ - carbomethoxypropionylbutylaminophenyl) - benztriazole,

2 - ($2^1$ - hydroxy - $5^1$ - $\beta$ - carbocyclohexyloxypropionylbutylaminophenyl) - benztriazole,

2 - ($2^1$ - hydroxy - $5^1$ - $\beta$ - carboallyloxypropionylbutylaminophenyl)-benztriazole.

In an analogous manner, from the reaction product of succinic acid anhydride and N-cyclohexyl - *p* - aminophenol, 2 - ($2^1$-hydroxy - $5^1$ - $\beta$ - carboxypropionylcyclohexylaminophenyl)-benztriazole is obtained.

*IV.*

Concentrated sodium hydroxide solution is added to 181 parts of N-carboxyethyl-*p*-aminophenol, obtained by alkaline saponification of the addition product of acrylonitrile and *p*-aminophenol, in 300 parts by volume of water until the solution obtained has a pH of 5.4. 141 Parts of benzoyl chloride are then added while stirring well, the pH being kept at 5.4 by the addition of concentrated sodium hydroxide solution. The reaction mixture is stirred overnight, the pH value being maintained. The product which separates is filtered off and recrystallised from glacial acetic acid/water (M.P. 192°).

229 Parts of this benzoyl product is coupled in a neutral solution with 113 parts of diazotised 97.9% *o*-nitroaniline. The still moist azo dyestuff obtained is dissolved in 2000 parts by volume of 2 N sodium hydroxide solution. 200 Parts of zinc dust are added within 5 minutes, care being taken by cooling that the temperature does not exceed 35°. The mixture is stirred at this temperature until it becomes greenish yellow. The 2 - ($2^1$ - hydroxy - $5^1$ - N - $\beta$ - carboxyethyl - benzoylaminophenyl) - benztriazole is precipitated by the slow addition of 700 parts by volume of concentrated hydrochloric acid. M.P. 187° (from glacial acetic acid/water).

This carboxy compound is converted by known methods into its acid chloride and this is refluxed for 1 hour with three times the amount by weight of n-butanol. The ester which crystallises on cooling can be recrystallised from butanol/ligroin. M.P. 123°.

On using methanol, cyclohexanol, benzyl alcohol or decanol instead of the butanol, the following compounds are obtained:

2 - ($2^1$ - hydroxy - $5^1$ - benzoyl - $\beta$ - carbomethoxy - ethylaminophenyl) - benztriazole,

2 - ($2^1$ - hydroxy - $5^1$ - benzoyl - $\beta$ - carbocyclohexyloxy - ethylaminophenyl) - benztriazole,

2 - ($2^1$ - hydroxy - $5^1$ - benzoyl - $\beta$ - carbobenzyloxy - ethylaminophenyl) - benztriazole,

2 - ($2^1$ - hydroxy - $5^1$ - benzoyl - $\beta$ - carbodecyloxy - ethylaminophenyl) - benztriazole.

*V.*

11.3 Parts of 2-($2^1$-hydroxy-$5^1$-aminophenyl)-benztriazole are stirred with 6.1 parts of dimethyl aniline and 120 parts by volume of solvent. 8.2 Parts of chlorocarbonic acid cyclohexyl ester dissolved in 80 parts by volume of chlorobenzene are added dropwise to the suspension obtained while stirring well. The thick slurry obtained is stirred for half an hour on an oil bath at an inner temperature of 138—140°. After cooling, the crystalline product is filtered off under suction, and washed well with methanol and ligroin. After drying, it is recrystillised several times from a mixture of chlorobenzene/toluene. The 2-($2^1$-hydroxy - $5^1$ - carbocyclohexyloxyaminophenyl)-benztriazole, which crystallises in white needles, melts at 194°.

The following substances are obtained in an analogous manner:

2 - ($2^1$ - hydroxy - $5^1$ - carbocyclohexyloxyaminophenyl) - 5 - chlorobenztriazole,

2 - ($2^1$ - hydroxy - $5^1$ - carbocyclohexyloxycyclohexylaminophenyl) - benztriazole,

2 - ($2^1$ - hydroxy - $5^1$ - carbocyclohexyloxymethylaminophenyl)-benztriazole,

2 - ($2^1$ - hydroxy - $5^1$ - carbocyclohexyloxyaminophenyl) - 5 - methoxy - 6 - methylbenztriazole,

2 - ($2^1$ - hydroxy - $5^1$ - carbocyclohexyloxyaminophenyl) - benztriazole - 5-carboxylic acid butyl ester,

2 - ($2^1$ - hydroxy - $3^1$ - phenyl - $5^1$-carboxycyclohexyloxyaminophenyl) - benztriazole-5-sulphonic acid dibutylamide,

2 - ($2^1$ - hydroxy - $3^1$ - phenyl - $5^1$ - carbocyclohexyloxyaminophenyl) - benztriazole-5-ethyl sulphone.

*VI.*

7.7 Parts of 2-(2¹-hydroxy-5¹-aminophenyl)-benztriazole are stirred with 50 parts by volume of *o*-dichlorobenzene, 4.2 parts of dimethyl aniline and 9.9 parts of 2-chloro-4,6-dibutylmercapto-s-triazine and, after slowly heating, are refluxed for 2½ hours. After cooling, the dichlorobenzene is removed from the reaction mixture with steam. The viscous oil which remains, after pouring off the water, is stirred with a little ethanol whereupon it slowly crystallises. Repeated recrystallisation from ethanol produces the pale yellowish 2-[2¹ - hydroxy - 5¹ - (4¹¹,6¹¹ - dibutylmercapto - s - triazinyl - (2¹¹)) - aminophenyl]-benztriazole which melts at 112°.

The following products are obtained by the same procedure:

2 - [2¹ - hydroxy - 5¹ - (4¹¹,6¹¹ - dibutyloxy-s - triazinyl - (2¹¹)) - aminophenyl]-benztriazole,

2 - [2¹ - hydroxy - 5¹ - (4¹¹,6¹¹ - dioctylmercapto - s - triazinyl - (2¹¹)) - aminophenyl]-benztriazole,

2 - [2¹ - hydroxy - 5¹ - (4¹¹,6¹¹ - bis - methylcyclohexylamino - s - triazinyl - (2¹¹))-aminophenyl]-benztriazole,

2 - [2¹ - hydroxy - 5¹ - (4¹¹,6¹¹ - dibenzylmercapto - s - triazinyl - (2¹¹)) - aminophenyl]-benzotriazole,

2 - [2¹ - hydroxy - 5¹ - (4¹¹,6¹¹ - bis-diethylamino - s - triazinyl - (2¹¹))-aminophenyl]-benztriazole,

2 - [2¹ - hydroxy - 5¹ - (4¹¹,6¹¹ - bis-benzylamino - s - triazinyl - (2¹¹))-aminophenyl]-benztriazole,

2 - (2¹ - hydroxy - 5¹ - 4¹¹ - dibutylamino-6¹¹ - chloropyrimidyl - (2¹¹) - aminophenyl)-benztriazole,

2 - (2¹ - hydroxy - 5¹ - 2¹¹ - butoxy - 5¹¹,6¹¹-dichloropyrimidyl - (4¹¹) - aminophenyl)-benztriazole,

2 - (2¹ - hydroxy - 5¹ - 4¹¹ - cyclohexylmercapto - 5¹¹,6¹¹ - dichloropyrimidyl-(2¹¹)-aminophenyl)-benztriazole.

*VII.*

33.9 Parts of 2-(2¹-hydroxy-5¹-aminophenyl)-benztriazole, 17.7 parts of benzaldehyde and 100 parts by volume of o-dichlorobenzene are stirred and slowly brought to the boil. At an inner temperature of about 175° 40 parts by volume of dichlorobenzene are slowly distilled off, the water formed also being azeotropically distilled off. After cooling the reaction mixture, the product is filtered off under suction and recrystallised from chlorobenzene. The 2-(2¹-hydroxy-5¹-benzalamidophenyl)-benztriazole melts at 158°.

31.4 Parts of this product in 240 parts by volume of pure dioxan are hydrogenated at room temperature and slight excess pressure in the presence of 10 parts of Raney nickel. After 2240 parts by volume of hydrogen have been taken up (which takes about 3 hours), hydrogenation is broken off. The hydrogen is replaced by nitrogen, the reaction mixture, in which the hydrogenation product has precipitated, is heated in a water bath until, apart from the Raney nickel, a clear solution is obtained. This is then filtered over Hiflow. "Hiflow" is a Registered Trade Mark.

The product is precipitated still hot from the yellow filtrate by the slow addition of water. The 2 - (2¹ - hydroxy - 5¹ - benzylaminophenyl)-benztriazole so obtained melts at 143°.

Other carbonyl compounds are reacted in the same way. In the case of ketones e.g. cyclohexanone, an addition of anhydrous zinc chloride is recommended.

3.2 Parts of 2-(2¹-hydroxy-5¹-benzylaminophenyl)-benztriazole are stirred with 10 parts by volume of dry pyridine and 1.5 parts of methane sulphonic acid chloride are so added to this mixture that the temperature does not exceed 30°. The solution obtained is left to stand for 2 hours at room temperature and is then heated while stirring on a boiling water bath for 30 minutes. After cooling, the product is precipitated with water, filtered off under suction and recrystallised from glacial acetic acid and toluene. The 2 - (2¹ - hydroxy - 5¹ - methane sulphonic acid benzylamidophenyl)-benztriazole so obtained melts at 215° and is in the form of pale yellowish needles.

The following products are obtained in an analogous manner:

2 - (2¹ - hydroxy - 3¹ - methyl - 5¹ - methane sulphonic acid cyclohexylamidophenyl)-benztriazole-5-carboxylic acid allyl ester,

2 - (2¹ - hydroxy - 5¹ - methane sulphonic acid heptylamidophenyl) - 5 - chlorobenztriazole,

2 - (2¹ - hydroxy - 5¹ - methane sulphonic acid benzylamidophenyl) - benztriazole-5-sulphonic acid-γ-methoxypropylamide,

2 - (2¹ - hydroxy - 3¹ - chloro - 5¹ - methane sulphonic acid amidophenyl) - benztriazole-5-sulphonic acid dibutylamide.

*VIII.*

11.3 Parts of 2-(2¹-hydroxy-5¹-aminophenyl)-benztriazole, 6.2 parts of dimethyl aniline and 50 parts by volume of xylene (technical mixture) are stirred and a solution of 9.7 parts of chlorocarbonic acid octyl ester in 20 parts by volume of xylene is added dropwise to the suspension formed. The reaction mixture which solidifies into a thick slurry is heated to 138° inner temperature while stirring well whereupon a clear solution is formed. After cooling to 100°, the mixture in which crystals have already formed, is diluted with 50 parts by volume of ligroin and left to cool at room temperature.

The crystals which precipitate are filtered off under suction and well washed first with methanol, then with ligroin and finally with benzene. The product is recrystallised twice from toluene.

The 2 - ($2^1$ - hydroxy - $5^1$ - carbooctyloxy-aminophenyl)-benztriazole is obtained in the form of white crystals which melt at 142°.

The following products are obtained in an analogous manner:

2 - ($2^1$ - hydroxy - $5^1$ - carbophenoxyamino-phenyl)-benztriazole,
2 - ($2^1$ - hydroxy - $5^1$ - carbo - $\beta$ - butyl-mercaptoethoxyaminophenyl) - benz-triazole,
2 - ($2^1$ - hydroxy - $5^1$ - carbo - *o* - chloro-phenoxyaminophenyl)-benztriazole,
2 - ($2^1$ - hydroxy - $5^1$ - carbomethoxyamino-phenyl)-benztriazole,
2 - ($2^1$ - hydroxy - $5^1$ - carbo - *p* - methyl-phenoxyaminophenyl)-benztriazole,
2 - ($2^1$ - hydroxy - $5^1$ - carbo - $\beta$ - ethoxy-ethoxyaminophenyl)-benztriazole,
2 - ($2^1$ - hydroxy - $5^1$ - carbobenzyloxyamino-phenyl)-benztriazole,
2 - ($2^1$ - hydroxy - $5^1$ - carbo - $4^{11}$ - methyl-cyclohexyloxyaminophenyl)-benztriazole,
2 - ($2^1$ - hydroxy - $5^1$ - carbo - *m* - methyl-benzyloxyaminophenyl)-benztriazole.

*IX.*

11.3 Parts of 2-($2^1$-hydroxy-$5^1$-amino-phenyl)-benztriazole, 6.1 parts of dimethyl aniline, 18.5 parts of 2-chloro-4,6-bis-di-butylamino-s-triazine and 50 parts by volume of *o*-dichlorobenzene are refluxed for 4½ hours (inner temperature 184—185°). After cooling, the *o*-dichlorobenzene is removed from the reaction mixture with steam. The resin which remains, after pouring off the aqueous phase, is kneeded with methanol whereupon the product slowly crystallises. On repeated recrystillisation from ethanol, 2-[$2^1$-hydroxy-$5^1$ - ($4^{11}$,$6^{11}$ - bis - dibutylamino - s - triazinyl-($2^{11}$)) - aminophenyl] - benztriazole is obtained as yellowish crystals which melt at 88°.

The following substances are obtained in an analogous manner:

2 - [$2^1$ - hydroxy - $3^1$ - methyl - $5^1$ - ($4^{11}$,$6^{11}$-bis - dibutylamino - s - triazinyl - ($2^{11}$))-aminophenyl]-benztriazole,
2 - [$2^1$ - hydroxy - $5^1$ - ($4^{11}$,$6^{11}$ - bis - di-butylamino - s - triazinyl - ($2^{11}$))-aminophenyl] - 5 - methoxy - 6-methyl-benztriazole,
2 - [$2^1$ - hydroxy - $5^1$ - ($4^{11}$,$6^{11}$ - bis - di-butylamino - s - triazinyl - ($2^{11}$))-aminophenyl] - 4,6 - dichloro - benz-triazole,
2 - [$2^1$ - hydroxy - $5^1$ - ($4^{11}$,$6^{11}$ - bis - di-butylamino - s - triazinyl - ($2^{11}$))-aminophenyl]-5-carboxy-benztriazole.

*X.*

7.4 Parts of caproic acid chloride dissolved in 50 parts by volume of chlorbenzene are slowly added to 12.0 parts of 2-($2^1$-hydroxy-$5^1$ - aminophenyl) - 5 - methyl - benz-triazole (M.P. 148°, produced according to Example 1), suspended in 100 parts by volume of dimethyl aniline. The addition is made at 30—37° while stirring well. The re-action mixture is then heated to 92—95° whereupon a clear solution is obtained. It is allowed to cool, while stirring, whereupon the product separates in crystalline form. After filtering off under suction, washing with methanol and recrystallising from methyl cellosolve, the 2-($2^1$-hydroxy-$5^1$-pentane carboxylic acid amidophenyl)-5-methyl-benztriazole melts at 193°.

The following products are obtained by an analogous process:

2 - ($2^1$ - hydroxy - $5^1$ - stearoylaminophenyl)-5-methyl-benztriazole,
2 - ($2^1$ - hydroxy - $5^1$ - oleylaminophenyl)-5-methyl-benztriazole,
2 - ($2^1$ - hydroxy - $5^1$ - methacryloylamino-phenyl)-5-methyl-benztriazole,
2 - ($2^1$ - hydroxy - $5^1$ - cyclohexane carboxylic acid amidophenyl)-5-methyl-benztriazole,
2 - ($2^1$ - hydroxy - $5^1$ - phenyl acetic acid amidophenyl) - 5 - methyl - benztriazole,
2 - ($2^1$ - hydroxy - $5^1$ - $\beta$ - butylmercapto-propionylaminophenyl) - 5 - methyl-benztriazole,
2 - ($2^1$ - hydroxy - $5^1$ - $\beta$ - ethoxypropionyl-aminophenyl)-5-methyl-benztriazole,
2 - ($2^1$ - hydroxy - $5^1$ - phenoxyacetylamino-phenyl)-5-methyl-benztriazole,
2 - ($2^1$ - hydroxy - $5^1$ - $\beta$ - phenylpropionyl-aminophenyl)-5-methyl-benztriazole,
2 - ($2^1$ - hydroxy - $5^1$ - cyclopentane carboxylic acid amidophenyl)-5-methyl-benztriazole,
2 - ($2^1$ - hydroxy - $5^1$ - *p* - methylphenoxy-acetylaminophenyl) - 5 - methyl - benz-triazole.

*XI.*

1.8 Parts of phenyl isocyanate are added while stirring to 3.2 parts of 2-($2^1$-hydroxy-$5^1$ - benzylaminophenyl) - benztriazole sus-pended in 15 parts by volume of *o*-dichloro-benzene and the mixture is refluxed for 10 minutes. On cooling the mixture, crystals slowly form which are filtered off under suction and washed with toluene. Repeated recrystallisation from a mixture of ligroin/chlorobenzene to which a few drops of ethanol have been added, produces 2-($2^1$-hydroxy - $5^1$ - N - phenylcarbamoylbenzyl-aminophenyl)-benztriazole in the form of white needles. The crystals melt at about 180° with decomposition.

On using corresponding starting materials, the following products are obtained:

2 - ($2^1$ - hydroxy - $3^1$ - methyl - $5^1$-N - phenylcarbamoylcyclohexylaminophenyl) - 5 - methyl - benztriazole,

2 - ($2^1$ - hydroxy - $5^1$ - N - phenylcarbamoylheptylaminophenyl) - 4,6 - dichlorobenztriazole,

2 - ($2^1$ - hydroxy - $5^1$ - N - phenylcarbamoylmethylaminophenyl) - 5 - carboxylic acid butyl ester.

*XII.*

1.2 Parts of chloroacetic acid chloride are added while stirring well at room temperature to 3.2 parts of 2-($2^1$-hydroxy-$5^1$-benzylaminophenyl)-benztriazole suspended in 20 parts by volume of *o*-dichlorobenzene. On completion of the addition, the mixture is slowly heated whereupon the yellow colour of the suspension disappears and a white precipitate is formed. As soon as the yellow colour has completely disappeared 3 parts of dimethyl aniline are added to the mixture which immediately becomes yellow again. The mixture is then heated in a water bath until a clear solution is obtained and is then kept for 30 minutes on a boiling water bath. After cooling, the *o*-dichlorobenzene is removed from the reaction mixture in vacuo. The distillation residue is taken up in glacial acetic acid and allowed to crystallise out of the solution obtained. Recrystallisation twice from glacial acetic acid produces 2-($2^1$-hydroxy - $5^1$ - chloroacetylbenzylaminophenyl)-benztriazole in the form of coarse needles which melt at 185°.

On using the corresponding acid chlorides, the following products are obtained:

2 - ($2^1$ - hydroxy - $5^1$ - N,N - dimethylcarbamoylbenzylaminophenyl) - benztriazole,

2 - ($2^1$ - hydroxy - $5^1$,$1^{11}$ - morpholinocarbonylbenzylaminophenyl) - benztriazole,

2 - ($2^1$ - hydroxy - $5^1$ - $\beta$ - butoxypropionylbenzylaminophenyl) - benztriazole,

2 - ($2^1$ - hydroxy - $5^1$ - $\beta$ - benzylmercaptopropionylbenzylaminophenyl) - benztriazole,

2 - ($2^1$ - hydroxy - $5^1$ - $\beta$ - phenylmercaptopropionylbenzylaminophenyl) - benztriazole.

The chlorine atom of the 2-($2^1$-hydroxy-$5^1$ - chloroacetylbenzylaminophenyl) - benztriazole can easily be exchanged for amino groups; thus, for example, 2-($2^1$-hydroxy-$5^1$-N,N - diethylaminoacetylbenzylaminophenyl)-benztriazole is obtained.

*XIII.*

1.7 Parts of *p*-toluic acid chloride are added at room temperature to 3.2 parts of 2-($2^1$-hydroxy - $5^1$ - benzylaminophenyl) - benztriazole suspended in 15 parts by volume of Sanguajol. The mixture is heated according to Example XII and treated with dimethyl aniline. After cooling, 20 parts by volume of petroleum ether and 20 parts by volume of water are added to the two-phase reaction mixture whereupon, while stirring, the product crystallises. After filtering off under suction and washing with a little methanol, the 2 - ($2^1$ - hydroxy - $5^1$ - *p* - methylbenzoylbenzylamidophenyl) - benztriazole is recrystallised from aqueous acetic acid solution and, after drying well, from ligroin/chlorobenzene. Substantially colourless crystals are obtained which melt at 144°.

On using the corresponding acid chlorides, the following products are obtained:

2 - ($2^1$ - hydroxy - $5^1$ - *o* - chlorobenzoylbenzylaminophenyl)-benztriazole,

2 - ($2^1$ - hydroxy - $5^1$ - *p* - methoxybenzoylbenzylaminophenyl)-benztriazole,

2 - ($2^1$ - hydroxy - $5^1$ - *m* - methylbenzoylbenzylaminophenyl)-benztriazole,

2 - ($2^1$ - hydroxy - $5^1$ - *p* - methylphenylacetylbenzylaminophenyl)-benztriazole,

2 - ($2^1$ - hydroxy - $5^1$ - $\beta$ - phenylpropionylbenzylaminophenyl)-benztriazole.

*XIV.*

2.0 Parts of *p*-toluene sulphonic acid chloride are added to 2.3 parts of 2-($2^1$-hydroxy - $5^1$ - aminophenyl) - benztriazole suspended in 10 parts by volume of dry pyridine whereby the temperature is not allowed to rise over 30°. The mixture is stirred for 2 hours at room temperature and then refluxed for 10 minutes. The product is precipitated by the addition of 50 parts of water, filtered off under suction, washed with methanol and dried. Recrystallisation from methyl cellosolve/dimethyl formamide/water produces 2 - ($2^1$ - hydroxy - $5^1$ - *p* - toluene sulphonic acid amidophenyl)-benztriazole in the form of substantially colourless crystals which melts at 238°. "Cellosolve" is a Registered Trade Mark.

On using the corresponding sulphonic acid chlorides, the following substances are obtained:

2 - ($2^1$ - hydroxy - $5^1$ - benzene sulphonic acid amidophenyl)-benztriazole,

2 - ($2^1$ - hydroxy - $5^1$ - *o* - chlorobenzene sulphonic acid amidophenyl) - benztriazole,

2 - ($2^1$ - hydroxy - $5^1$ - *p* - methoxybenzene sulphonic acid amidophenyl) - benztriazole,

2 - ($2^1$ - hydroxy - $5^1$ - *p* - butylbenzene sulphonic acid amidophenyl) - benztriazole.

*XV.*

1.4 Parts of methane sulphonic acid chloride are added to 2.3 parts of 2-($2^1$-hydroxy - $5^1$ - aminophenyl) - benztriazole suspended in 15 parts by volume of *o*-di-

chlorobenzene. The mixture is heated according to Example XI and treated with dimethyl aniline. On completion of the reaction, the solvent is removed with steam and the water insoluble residue is washed well with methanol. Recrystallisation from methyl cellosolve/dimethyl formamide produces 2-($2^1$ - hydroxy - $5^1$ - methane sulphonic acid amidophenyl)-benztriazole in the form of almost colourless crystals which melt at 249°.

On using the corresponding sulphonic acid chlorides, the following products are obtained:

2 - ($2^1$ - hydroxy - $5^1$ - cyclohexane sulphonic acid amidophenyl)-benztriazole,

2 - ($2^1$ - hydroxy - $5^1$ - butane - $1^{11}$- sulphonic acid amidophenyl) - benztriazole,

2 - ($2^1$ - hydroxy - $5^1$ - allyl - sulphonic acid amidophenyl)-benztriazole,

2 - ($2^1$ - hydroxy - $5^1$ - benzyl sulphonic acid amidophenyl)-benztriazole.

*XVI.*

1.7 Parts of phenyl isocyanate are added to 2.4 parts of 2-($2^1$-hydroxy-$5^1$-aminophenyl) - 5 - methyl - benztriazole suspended in 10 parts by volume of *o*-dichlorobenzene and 10 parts by volume of dimethyl formamide and the mixture is heated for 30 minutes at 130°. After cooling, the 2-($2^1$-hydroxy - $5^1$ - N - phenylcarbamoylaminophenyl) - 5 - methyl - benztriazole crystallises into pale yellowish coarse needles which are washed well with ethanol. To further purify, the product can be suspended in methyl cellosolve and dissolved by the dropwise addition of concentrated sodium hydroxide solution. A slight excess of glacial acetic acid is added to the yellow solution so obtained at 90° whereupon the colour changes to pale yellow. On slowly cooling with stirring, the product separates out in very fine long needles which are well washed with methanol and then dried in vacuo. M.P. >280°. The substance decomposes at a higher temperature.

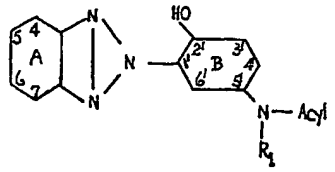
On using corresponding starting materials, the following substances are obtained:

2 - ($2^1$ - hydroxy - $5^1$ - N - *o* - ethylphenylcarbamoylaminophenyl) - 5 - methylbenztriazole, and

2 - ($2^1$ - hydroxy - $5^1$ - N - phenylthiocarbamoylaminophenyl) - 5 - methylbenztriazole.

WHAT WE CLAIM IS:—

1. Process for the stabilisation of light and oxidation sensitive organic material characterised by incorporating into this material a compound of the general formula I




(I)

wherein "Acyl" represents an organic acyl radical as hereinbefore defined, and

$R_1$ represents hydrogen or an alkyl, alkenyl, cycloalkyl, or aralkyl radical which can be substituted by a carboxy or carbalkoxy group, whilst $R_1$ and "Acyl" together with the amino nitrogen atom can form a ring and, in this case, $R_1$ represents a carbonyl group or a methylene group possibly substituted by alkyl groups, and

wherein the nucleus A can be substituted in the 4-, 5- and 6-positions by alkyl, alkoxy, carboxy, carboxylic acid ester, carboxylic acid amide, sulphonic acid amide and alkylsulphonyl groups or halogens, and

the nucleus B can be substituted in the $3^1$- and $4^1$-positions by alkyl, cycloalkyl, aralkyl and aryl groups or halogens.

2. Organic materials which contain as light and oxidation protecting agent, a compound of the general formula I given in claim 1.

3. Organic films or foils containing a UV-absorbing compound of the general formula I.

4. Organic material as claimed in claim 2 whenever obtained by a process hereinbefore particularly described.

5. Organic material as claimed in claim 2 as herein described with reference to and as illustrated in the foregoing Examples 1—11.

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